

# **An initial study on atmospheric pressure ion transport by laser ionization and electrostatic fields**

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## **Introduction:**

Reduction of carbon dioxide ( $\text{CO}_2$ ) and other gases concentration in air and other gases has been of great concern in various fields, e.g., control of indoor air quality by ventilation (Nabinger1994, Persily1997), greenhouse effect (Hansen1981), or contamination control of process gases for semiconductor manufacturing (Briesacher1991). Recently, behaviour of ions, radicals and molecular species have been studied for the purpose of gas cleaning and purification from gas stream by corona discharge (Ohkubo1994), surface discharge (Oda1997), and electron beam injection (Hirota1995). However these methods using high discharge energy turned out not to be effective for lowering the concentration of  $\text{CO}_2$  due to the high energy penalty and equipment capital cost, of current capture and concentration technologies in operation and under development.

As an alternative, ionization of residual molecules in gas phase at atmospheric pressure (API) has been proposed as a purification method for nitrogen (Briesacher1991). This approach is inspired in the atmospheric pressure ionization, by means of for example electron impact ionization, which has been successfully applied in mass spectrometry during the last decades. However due to the relatively low ionization yield produced, these techniques are limited to a very small amount of compounds, and ion currents in the range of nanoamps. However, Ita et al. applied successfully this idea for nitrogen purification with small amounts of different contaminants, being able to modify the concentration of impurities in the ppm range.

In order to get better purification capabilities it would be desirable to work with higher ion currents to perform separations of compounds in concentrations higher than the ppm range. In other words, to increase the ionization yields. Unfortunately there is almost no literature concerning this area of work, mainly because the formation of considerable amounts of ions in a reduced space leads to work with a very different situation than in the case of API.

Following the above discussed strategy, in some works a radioactive source was used for the ionization process (Ito2002a, Ito 2002b, Ito 2003, Ito 2004). This yielded a stable ionization of small amounts of gas for a long time but the ionization yield was again too low for the efficient separation of mixtures out of the ppm range. In this scenario it seems logical the implementation of laser radiation to achieve a high degree of ionization of the compound of interest. Additionally using different laser based ionization techniques the ionization can be potentially selective, i.e., it is possible to produce exclusively the ionization of a target molecule from a complex mixture.

Based on the discussed above, the goal of this work is to develop a prototype to study the implementation of laser based ionization techniques and the subsequent evolution and transport of the generated ions by means of electrostatic fields.

### Experimental Setup:

As indicated previously in this work we have explored the possibility of using laser radiation as a source of ionization for the ion transport studies. Since the ionization depends strongly on the peak intensity, for obtaining an efficient ionization of the target sample, it is much more convenient to work with pulsed laser rather than with continuous wave (CW) ones. Concretely in this work the pulses used in this work were in the femtosecond time regime ( $1\text{ fs}=10^{-15}\text{ s}$ ). These pulses were generated by a commercial Ti:Sapphire laser (Newport-Spectra Physics Spitfire ACE Pro) system which delivers pulses of 120 fs, at a wavelength of 800 nm, with repetition rate of 1 KHz and energy per pulse up to 7 mJ.

The generated laser radiation was focalized by different lenses with focals in the order of tens of centimeters into a homemade prototype designed specifically for this work (PCTES2013070325). The focal spot was always at the center of the prototype. This is schematically shown in Figure 1. The prototype has basically the same structure like the one described in *Ito et al, 2002*. It consists of two circular electrodes separated a distance of 4 mm that surround the ionization region X-axis, while the Y-axis holds the optical path for the laser, and the Z-axis the gas flow. The voltage applied to the electrodes for extracting the generated ions from the gas flow was provided by two power supplies N5772A (600V, 2.6A, 1560W, Agilent) connected in serial array.

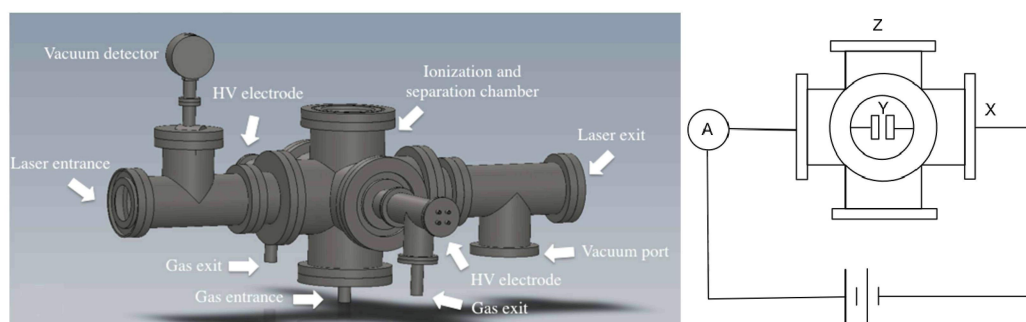


Figure 1: Simplified view of the prototype

## Results and discussion:

As it was said before, the main goal of this work is to check the feasibility of the use of laser radiation as the ionization source, and to establish the main parameters that are relevant to the system. Since the laser radiation used is in the infrared (IR) range the ionization is produced by the simultaneous absorption of the necessary number of photons  $n$  to overcome the ionization potential (IP) of the molecule. This process is highly nonlinear, and with a significantly low cross section, depending the ionization signal with respect to the intensity as:

$$Signal \propto I^n$$

Hence, it is necessary the focalization of the laser for achieving high laser intensities in the interaction region, and therefore large ionization signals.

When working with fs laser systems multiphoton process is not the only ionization process that must be taken into account. Usually the intensity in the focal spot is so large that the Coulomb potential created by the nucleus is distorted, being possible the ejection of an electron through tunneling. This mechanism is known as *tunneling ionization*, or if the deformation of the Coulomb potential is so large that the bound electron can freely escape *over barrier ionization*. The parameter that distinguishes between both regimes is the Keldysh parameter

$$\gamma = \omega_L \sqrt{\frac{2 IP}{I_L}}$$

where  $\omega_L$  is the laser frequency. If  $\gamma > 1$  multiphoton ionization rules the ionization process while for  $\gamma < 1$  tunneling or over barrier ionization the main mechanism. It is important to mention that the Keldysh factor must be taken as a rule of thumb because there is not an abrupt transition between the different mechanisms, being usually all of them present for ionizations with femtosecond laser radiation.

It is important also to notice that the focalization of fs pulses in air produces the filamentation of the laser (see Fig. 2). In simple words, filamentation is a competing effect between self focusing, produced by the dependence of the refractive index of air with respect to the intensity, and the defocalizing effect induced by the generated plasma by such concentration of energy. Both effects together produced the propagation of the laser beam through the medium without distortion. In air the critical power  $P_c$ , i.e., the power for which self focusing starts to play a role in the propagation of a laser beam, is around 1.9 GW. Also it is important to mention that the electron density within the filament is fixed to a value of around  $5.3 \cdot 10^{16} \text{ cm}^{-3}$  [Chin2012].

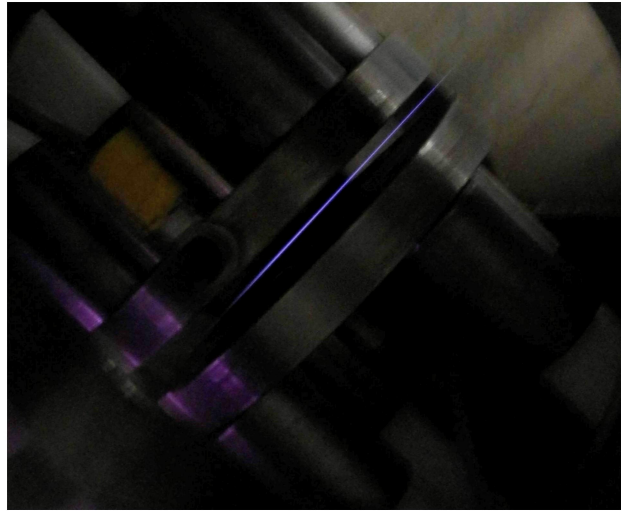


Figure 2: Filament inside the prototype

It must be mentioned that in order to define the best laser characteristics for this work experiments with a nanosecond laser system were also carried out. With nanosecond lasers since the pulse is long and the plasma formation takes place in the early stages of the pulse, the laser-plasma interaction time is very long. This produces a very hot and dense plasma opaque to the laser radiation that reduces dramatically the current of ions.

Figure 3 shows the current received in the electrodes as a function of the voltage across them for different lenses and for a fixed energy per pulse of the laser at atmospheric pressure. When the voltage was set to 0 V, no intensity was detected in the amperimeter (see Fig. 1), but as the voltage increased, a small current supplied by the power supply was needed to keep the potential difference stable. This clearly indicated that ions were reaching the electrodes where they neutralized. Thus measuring this current it was possible to have direct access to the number of ions collected. As it can be seen in Fig. 3 the current grows almost proportionally to the applied voltage.

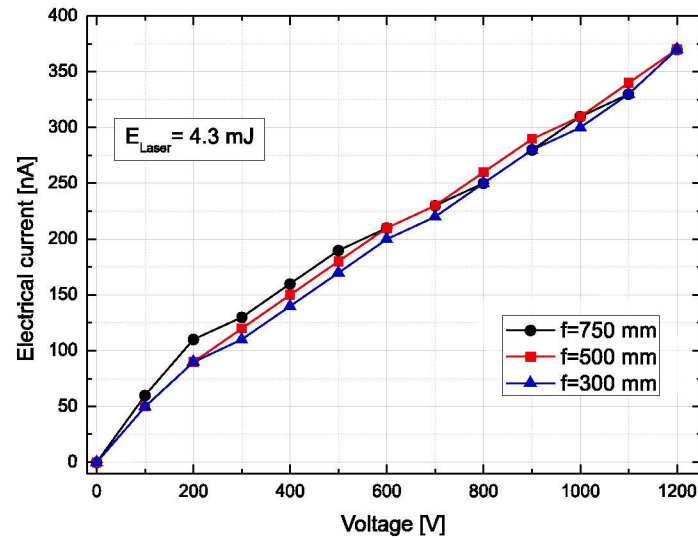


Figure 3: Electrical current versus applied voltage in the electrodes for different focal lengths at atmospheric pressure.

It is important to point out that although the data showed in Fig. 3 indicates that it is possible to ionize and to transport the ions to the electrodes in the above conditions, the current obtained was not as high as expected when one considers the energy per laser pulse used for ionization. In our opinion the most plausible explanation is that the ionization energy was lost by recombination of the ions due to the high pressure of the system. Under these conditions the mean free path of the positive ions is very small and collisions lead to neutralization on their path to the electrode. To test this hypothesis, the prototype was closed and light vacuum was applied. The internal pressure of the system was set at 0.47 mbar. Figure 4 shows the obtained current as a function of the voltage across the electrodes for these experimental conditions. In both cases a significantly more intense current was detected, saturating rapidly for a voltage across the electrodes of around 50 V.

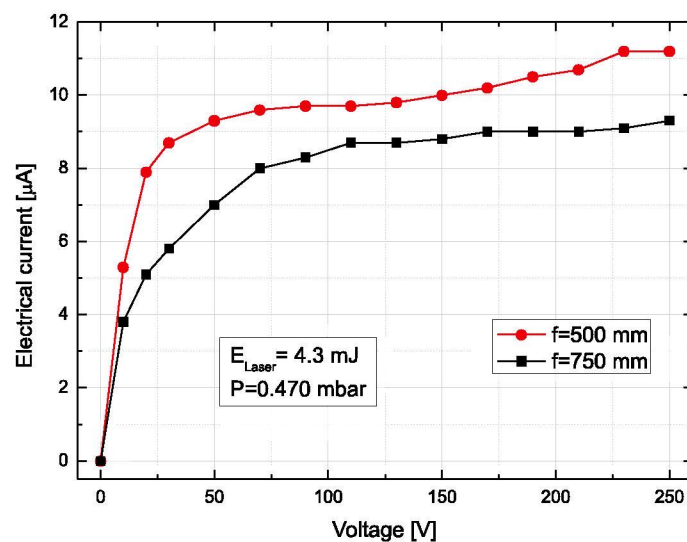


Figure 4: Electrical current versus applied voltage in the electrodes for different focal lengths in vacuum.

Very valuable information can be obtained when Figs. 3 and 4 are compared. As it was mentioned before the electron density within the filament is around  $5.3 \cdot 10^{16} \text{ cm}^{-3}$ . Hence, taking into consideration the dimensions of the produced filament, a cylinder with radius of  $100 \text{ }\mu\text{m}$  and length of  $2.8 \text{ cm}$ , and the repetition rate of the laser system ( $1 \text{ KHz}$ ), one can easily calculate the maximum possible measurable current resulting a value of  $7.5 \text{ mA}$ . The latter value is considerable bigger than the obtained values of Fig. 3, which range in the order of hundreds of nA.

When the pressure is decreased to  $0.470 \text{ mbar}$ , the density of air is also reduced to a value of  $1.2 \cdot 10^{16} \text{ particle/cm}^3$ . Taking this value as the maximum electron density within the filament, the maximum possible measurable current is  $1.7 \text{ mA}$  which is still far from the results obtained in Fig. 4. Two main hypotheses can be drawn to explain this discrepancy. On one hand in their way to the electrode the charged particles suffer collisions that produce their recombination. This hypothesis is supported by the fact that reducing the pressure, i.e., increasing the mean free path of the charged particles, the measured current in the electrodes is improved by a factor 100. But this hypothesis still cannot satisfactorily explain the difference between the theoretical expected current and the obtained one as well as the saturation in the obtained current in Figure 4.

On the other hand, another fact that must be taken into account for getting a whole picture of the problem is that a plasma is formed in the ionization region. Although the density of this plasma is of the order of  $10^{16} \text{ cm}^{-3}$  [Chin2012] and it is considered to be underdense, i.e., transparent to  $800 \text{ nm}$  radiation, ions and electrons are strongly correlated not being possible therefore to separate them. When an electric field is applied to the plasma, this gets polarized inducing a zone of zero electric field within it. Even so, electrons and ions, the latter much slower because of its higher mass, escape from the boundaries of the plasma reducing accordingly its density. This “particle leak” depends on the applied voltage, this is why for zero voltage there is no electric current measured, and also on the internal electric field induced by the external voltage. In our opinion, the combination of both effects, together with the possible recombination within the trip of the charge particle to the electrode (see above) are the main responsible of the experimental data showed in Figs. 3 and 4. It is important to mention that plasma dynamics is in general a very complex problem and is far beyond the scope of the present paper where a qualitatively explanation has been given. We are actually working in a more detailed description.

Figure 5 shows the obtained current as a function of the pressure in the prototype. As it was predicted above, pressure is a main parameter to control, not only because of the recombination rate of the ionized particles, but also because of the dynamics of the boundaries of the plasma created by the filament.

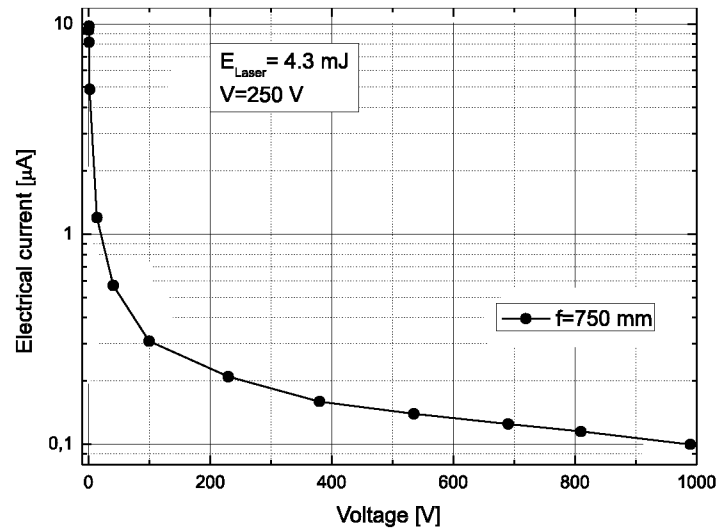


Figure 5: Electrical current as a function of the pressure inside the prototype.

In a next step, the goal was to explore the possibilities of increasing the ion transmission under atmospheric pressure. For this different approaches can be taken. The easiest one is to reduce the distance between the electrodes, reducing therefore the distance that the charged particles have to travel before reaching the electrodes. Although this option according with our previous discussion will increase the efficiency of the prototype, it is not an option because the prototype is intended to have a quantitative use. In other words, it has to allow the pass of relevant amounts of gas between the electrodes. A different alternative is to modify the characteristics of the ionization process. Figure 6 shows the produced current versus the voltage between electrodes for a spherical and a cylindrical lens under the same experimental conditions. A cylindrical lens focuses the light into a line rather than into a point like the spherical one. According to the experimental results, although the cylindrical lens provides an extended focus, i.e., a larger interaction area, than a spherical one, the produced current is reduced. The latter can be explained if one takes into account that the multiphoton ionization processes are highly nonlinear, depending strongly on the intensity in the interaction region and the peak intensity achievable by a cylindrical lens at the focal spot is much smaller than for a spherical one. To overcome the latter problem, more energy per pulse could be used so the ionization is saturated. Unfortunately this was not possible with the laser system used in this work.

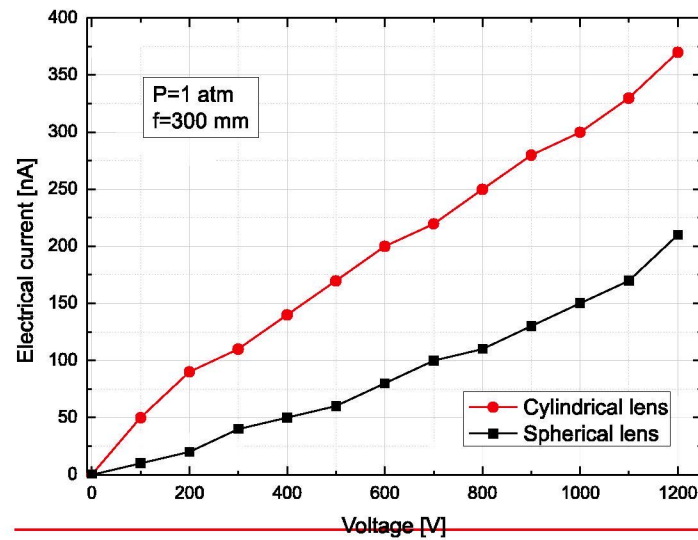


Figure 6: Electrical current as a function of the voltage for a spherical and a cylindrical lens.

Up to now all the experimental data described were taken under stationary conditions, but the design of the prototype was intended to be use for a continuous flow. Accordingly Fig. 7 shows the influence of introducing a drift velocity in the gas in the obtained current. This set of experiments was carried out in an atmosphere of nitrogen for experimental convenience. As it can be seen the results with a flow are slightly better than the one with a static atmosphere. A first hypothesis is that a drift velocity increases the mean free path of the charged particles, although this velocity is relatively small when compared with the thermal speed. At the moment we are carrying out different experiments to verify this idea.

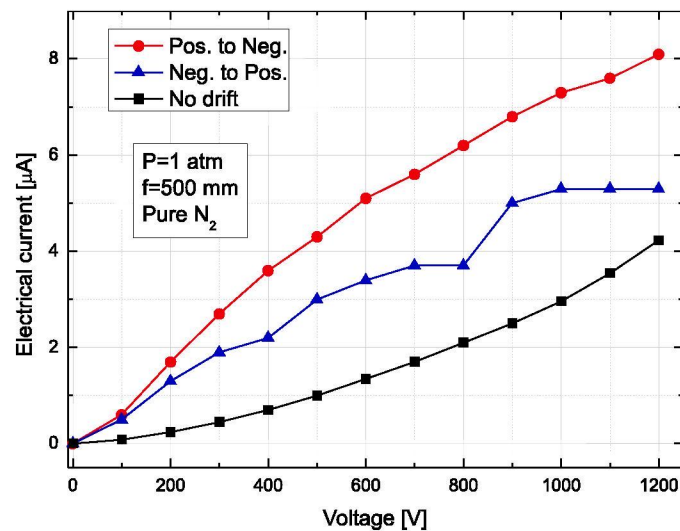


Figure 7: Electrical current versus voltage for an atmosphere of  $N_2$  and different drift velocity conditions.

The most interesting fact that can be deduced from Fig. 7 is that all currents are higher than those obtained with air in similar experimental conditions. For a better comparison Fig. 8 shows the obtained current for  $N_2$  and air. It is important to point out that the intensity



reached at the focal spot is sufficient for the ionization of all the species of air. Thus the dramatic difference between air and pure nitrogen emerges from the different processes of recombination of the ionized particles that take place once the laser pulse is gone.

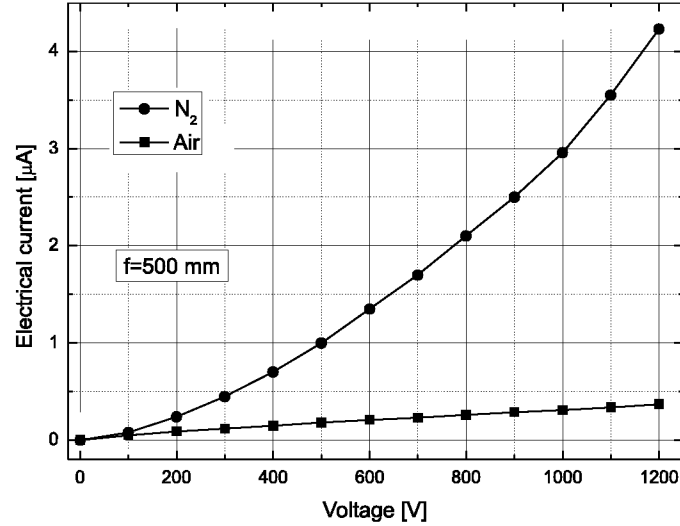


Figure 8: Electrical current versus voltage for air and N<sub>2</sub>

Since the second most abundant molecule in air is oxygen, it is tentative to study the dynamics followed by this molecule once is ionized. It is well known that at the laser intensities used in this work, molecular oxygen photodissociates through the Schumann band producing two atoms of oxygen [Farnamara1999, Peralta2009, Trushin2011, Peralta2013]. One of these atoms joins rapidly with another molecule of oxygen forming ozone (O<sub>3</sub>). Ozone results to be a very stable molecule, and it can act like a reservoir of energy during the recombination processes that take place in the plasma. To verify this hypothesis it would be necessary to have a detailed temporal analysis of the plasma recombination dynamics. This implies a specific experimental campaign due to the intrinsic difficulties (see above) for getting information about the dynamics of the plasma. This study will be matter of a near future publication.

## Conclusions:

In this article we have presented an initial analysis of the ionization and ion transport prototype of gases at atmospheric pressure. While results are not as high as desirable, they show that it is possible to generate and transport ions at atmospheric pressure. The fact that gas composition is relevant in the ion transmission opens a field to achieve separation of gases.

We have shown by measuring of electric current in the voltage source that we can follow the transmission of the ions at atmospheric pressure conditions when the laser ionized them. In addition, we have shown what initial composition of atmosphere for ionization is important in the final performance of process. Furthermore the geometry of the atmospheric separation unit by photoionization and electrostatic separation affect in the system performance. The gas

flow is essential for the ions transmissions. The shape of the electrode has an important role in our separation process.

Finally it is important to recognize here the complexity of this work because concepts from laser ionization, laser propagation (filamentation), mass spectrometry, and plasma dynamics must be taken into account for a complete understanding of the different processes that take place. We hope that our system and this work will help to stimulate more studies in such complex field (some of them are being carrying out at the moment), so in a near future we can use this technology to remove efficiently a target molecule from a complex sample at atmospheric pressure.

**Acknowledgments:**

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